Supporting Information

Hydrogen Tunneling in Protonolysis of Palladium(II) and Platinum(II) Methyl Complexes: Mechanistic Implications

John E. Bercaw,* George S. Chen, Jay A. Labinger,* and Bo-Lin Lin

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA

General Information: All air and/or moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques, or in a glove box under a nitrogen atmosphere. TFE-d_3 was purchased from Cambridge Isotope Laboratories and dried over 3 Å molecular sieves for at least 5 days, then vacuum distilled onto $B(C_6F_5)_3$, and shortly thereafter distilled into a Strauss flask. TFA-d_1 was purchased from Cambridge Isotope Laboratories and stored under nitrogen in the glove box. DCE-d_4 was purchased from Cambridge Isotope Laboratories and used immediately after the cap was opened. CD_2Cl_2 and $CDCl_3$ were dried over Na_2SO_4 just before use. $(COD)Pt(CH_3)_2$ was purchased from Strem Chemicals and stored under nitrogen in the glove box. A modified literature procedure was used for the synthesis of N,N,N',N'-tetramethyl-*trans*-cyclohexenediamine.[1] Compounds **1a**, **1c** and **1d** were synthesized according to literature procedures.[2] All other chemicals are commercially available and used as received without further purification. All NMR tubes were dried overnight in a 180 ºC oven. Protonolysis studies were performed in a screw cap NMR tube with a PTFE/silicone septum. The error introduced by residual protons from the glass surface of NMR tubes was found to be negligible by ^{1}H NMR spectroscopy with internal standard (within ^{1}H NMR error). All NMR spectra were recorded at room temperature using a Varian Mercury 300 spectrometer. NMR spectra were referenced to TMS using the residual impurities of the given solvent. Chemical shifts are reported using the standard δ notation in parts per million (positive chemical shifts are to a higher frequency from TMS), and coupling constant are reported in Hz. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), broad resonance (br). The Caltech X-ray Crystallography Laboratory provided the X-ray analysis.

Synthesis of Compound 1b: $(TMEDA)Pd(CH_3)_2$ (0.5 g, 2 mmol) and N,N,N',N'-tetramethyl-*trans*-cyclohexenediamine (3.4 g, 20 mmol) were added to a 20 ml vial. Benzene (10 mL) was added, and the reaction mixture was stirred for about 80 minutes, at which point colorless crystals were observed. The crystals were collected and washed with Et_2O. Recrystalization in CH_2Cl_2/Et_2O gave crystals suitable for X-ray diffraction analysis. Yield: 0.318 g, 55%. ^{1}H NMR (300 MHz, acetone-d_6) δ 2.6 – 2.7 (m, 2H), 2.49 (s, 6H), 2.36 (s, 6H), 1.6-1.8 (br m, 8H), -0.37 (s, 6H).

Protonolysis of 1a-c: A stock solution of 20:1 TFE-d_3/TFE-d_0 was prepared in the glove box and the ratio was confirmed by comparison of ^{1}H NMR peaks using an internal standard. A known amount of **1a-c** was dissolved in CD_2Cl_2 or $CDCl_3$ (0.7 mL) and transferred to a screw cap NMR tube sealed with a PTFE/silicone septum. A large excess amount of the 20:1 TFE-d_3/TFE-d_0 solution was then slowly transferred into the NMR tube by syringe. The NMR tube was then shaken manually to homogenize the mixture. The reactions of all three compounds were instantaneous and bubbles were observed upon mixing. ^{1}H NMR spectroscopy was used to

analyze the products (**2a-c**) and the CH_4/CH_3D ratios (~1 for all three cases). ^{1}H NMR data of the (methyl)(trifluoroethoxy)Pd^{II} complexes are similar to those previously reported.[3] The Pd-OCH_2CF_3 signal is absent due to exchange with excess TFE-d_3. Ethane formation was also observed by ^{1}H NMR spectroscopy, although the corresponding palladium products were not characterized. In all cases, no precipitates were observed. Protonolysis of **1a** was also performed in neat TFE-d_3, giving a ~ 1:4 mixture of CH_4/CH_3D.

Compound 2a: ^{1}H NMR (300 MHz, DCE-d_4) δ 2.66-2.43 (m, 4H), 2.56 (s, 6H), 2.47 (s, 6H), 0.29 (s, 3H).

Compound 2b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 – 2.65 (m, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H), 1.89 (m, 4H), 1.32 – 1.00 (m, 4H), 0.19 (s, 3H). ^{1}H NMR (300 MHz, TFE-d_3) δ 2.4-2.7 (m, 2H), 2.59 (s, 3H), 2.57 (s, 3H), 2.51 (s, 3H), 2.42 (s, 3H), 1.7-2.1 (m, 4H), 1.0-1.35 (m, 4H), 0.26 (s, 3H).

Compound 2c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.19 (dd, J = 1.5, 4.8, 1H), 8.90 (dd, J = 1.4, 5.2, 1H), 8.53 (dd, J = 1.4, 8.2, 1H), 8.45 (dd, J = 1.5, 8.2, 1H), 7.95 (m, 2H), 7.87 – 7.81 (m, 2H), 1.10 (s, 3H).

Protonolysis of 1d: Stock solutions of 20:1 TFE-d_3/TFE-d_0 and dimethylpalladium(II) **1d** (15 mg) in DCE-d_4 (2.3 ml) were prepared in the glove box in glass vials with PTFE/silicone septa. The vials with the stock solutions were then placed in an ice or oil bath with three screw cap NMR tubes sealed with PTFE/silicone septa at a constant temperature (273 K, 294 K, 311 K, 331 K). After the solutions were given a few minutes to equilibrate, the TFE-d_3/TFE-d_0 mixture (0.2 mL) and **1d**/DCE-d_4 solution (0.7 mL) were slowly transferred into the NMR tubes by syringes. After quickly shaking the tubes outside the bath to homogenize the mixtures, the NMR tubes were inserted back into the bath. The solutions were kept in the bath for a few more minutes before taking out for NMR analysis. The average CH_4/CH_3D ratios of three runs at each temperature were used. NMR data for **2d** are consistent with those reported for analogous systems.[4] The Pd-OCH_2CF_3 signal is absent due to exchange with excess TFE-d_3. ^{1}H NMR (300 MHz, $C_2D_4Cl_2$) δ 7.81 – 7.40 (m, 20H), 2.54 – 2.01 (m, 4H), 0.52 (br d, $^3J_{P\text{-}H}$ = 6.0, 3H).

Protonolysis of 3: A procedure analogous to **1d** was used for the protonolysis of **3**. A 10:1 TFA-d_1/TFA-d_0 mixture was used as the acid source. Data were acquired at 5 different temperatures (273 K, 294 K, 313 K, 333 K, 353 K). The average CH_4/CH_3D ratios of three runs at each temperature were used. NMR data for **4** are consistent with those reported for analogous systems.[5-6] ^{1}H NMR (300 MHz, $C_2D_4Cl_2$) δ 5.43 (m, 2H), δ 4.63 (m, 2H), δ 2.61-2.12 (m, 8H), δ 0.73 (s, $^2J_{Pt\text{-}H}$ = 65, 3H),

References:

1. Chooi, S. Y.; Tan, M. K.; Leung, P.H.; Mok, K. F. *Inorg.Chem.* **1994**, *33*, 3096.

2. de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

3. Kapteijn, G. M.; Dervisi, A.; Grove, D. M.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc*. **1995**, *117*, 10939-10949.

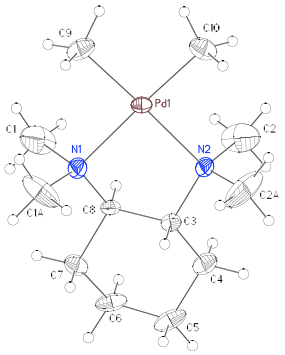
4. Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182-2188.

5. Komiya, S.; Mizuno, Y.; Shibuya, T. *Chem. Lett*. **1986**, 1065-1068.

6. Klein, A.; Klinkhammer, K.; Scheiring, T. *J. Organomet. Chem*. **1999**, *592*, 128-135.

Crystal Structure Analysis of 1b

Contents



1b

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 263612.

Table S1. Crystal data and structure refinement for 1b (CCDC 263612).

Empirical formula	$C_{12}H_{28}N_2Pd$
Formula weight	306.76
Crystallization Solvent	Benzene
Crystal Habit	Fragment
Crystal size	0.22 x 0.19 x 0.10 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 6839 reflections used in lattice determination	2.32 to 37.02°
Unit cell dimensions	a = 8.7968(4) Å b = 14.4109(6) Å c = 10.9609(5) Å
Volume	1389.51(11) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$Cmc2_1$
Density (calculated)	1.466 Mg/m^3
F(000)	640
Data collection program	Bruker SMART v5.630
θ range for data collection	2.71 to 42.65°
Completeness to θ = 42.65°	95.3 %
Index ranges	$-15 \le h \le 16$, $-27 \le k \le 27$, $-20 \le l \le 15$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	16623
Independent reflections	4181 [R_{int}= 0.0732]
Absorption coefficient	1.311 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8801 and 0.7613

Table S1 (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4181 / 1 / 101
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.379
Final R indices [$I>2\sigma(I)$, 3385 reflections]	R1 = 0.0415, *w*R2 = 0.0743
R indices (all data)	R1 = 0.0553, *w*R2 = 0.0769
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.05(5)
Largest diff. peak and hole	3.139 and -1.635 e.Å^{-3}

Special Refinement Details

The molecule occupies a special position in the unit cell, a mirror plane at x=1. Several atoms (Pd1, N1, N2, C4, C7, C9 and C10) actually sit on the mirror; see Table 2 for atoms with a x-coordinate identically 1. The mirror creates the appropriate methyl groups associated with C1 (C1A) and C2 (C2A) to give a complete molecule; see figure. All other atoms lie above or below the mirror as appropriate for the pucker in the ring.

Peaks (and holes) on the final difference Fourier that are stronger than one electron lie within 0.8Å of Pd.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S1. Molecular structure of complex 1b

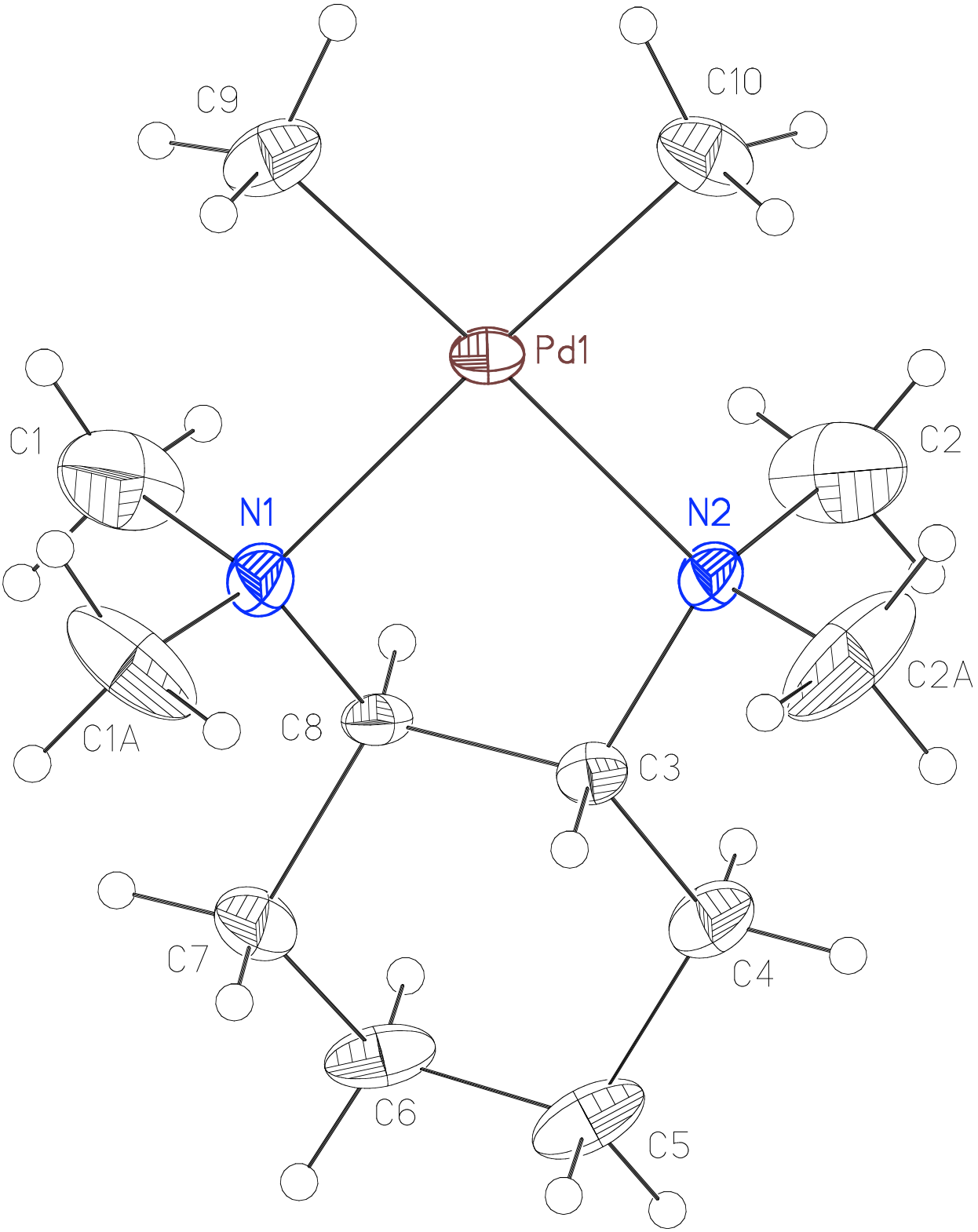


Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1b (CCDC 263612). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	10000	7420(1)	7859(1)	18(1)
N(1)	10000	6502(4)	6263(4)	24(1)
N(2)	10000	8500(4)	6445(5)	21(1)
C(1)	8657(5)	5905(3)	6273(4)	57(1)
C(2)	8651(5)	9084(3)	6572(4)	67(2)
C(3)	10385(5)	8034(3)	5249(4)	18(1)
C(4)	10000	8639(3)	4128(4)	31(1)
C(5)	10425(5)	8153(3)	2932(10)	35(1)
C(6)	9528(5)	7244(3)	2872(15)	33(1)
C(7)	10000	6618(3)	3939(4)	29(1)
C(8)	9576(5)	7095(3)	5165(4)	18(1)
C(9)	10000	6387(5)	9119(6)	33(2)
C(10)	10000	8308(5)	9280(7)	33(2)

Table S3. Selected bond lengths [Å] and angles [°] for 1b (CCDC 263612).

Pd(1)-C(10)	2.016(7)	C(1)#1-N(1)-C(1)	107.8(5)
Pd(1)-C(9)	2.031(7)	C(2)#1-N(2)-C(2)	108.6(6)
Pd(1)-N(1)	2.192(5)		
Pd(1)-N(2)	2.196(6)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,z

Table S4. Bond lengths [Å] and angles [°] for 1b (CCDC 263612).

Pd(1)-C(10)	2.016(7)	C(10)-Pd(1)-C(9)	86.5(3)
Pd(1)-C(9)	2.031(7)	C(10)-Pd(1)-N(1)	177.7(3)
Pd(1)-N(1)	2.192(5)	C(9)-Pd(1)-N(1)	95.80(19)
Pd(1)-N(2)	2.196(6)	C(10)-Pd(1)-N(2)	95.45(17)
N(1)-C(1)#1	1.462(5)	C(9)-Pd(1)-N(2)	178.0(3)
N(1)-C(1)	1.462(5)	N(1)-Pd(1)-N(2)	82.2(2)
N(1)-C(8)	1.522(6)	C(1)#1-N(1)-C(1)	107.8(5)
N(2)-C(2)	1.462(5)	C(1)#1-N(1)-C(8)	122.3(4)
N(2)-C(2)#1	1.462(5)	C(1)-N(1)-C(8)	97.9(3)
N(2)-C(3)	1.512(7)	C(1)#1-N(1)-Pd(1)	110.5(3)
C(3)-C(8)	1.531(6)	C(1)-N(1)-Pd(1)	110.5(3)
C(3)-C(4)	1.544(5)	C(8)-N(1)-Pd(1)	107.0(3)
C(4)-C(5)	1.533(11)	C(2)#1-N(2)-C(2)	108.6(6)
C(5)-C(6)	1.530(6)	C(2)-N(2)-C(3)	121.4(4)
C(6)-C(7)	1.534(12)	C(2)#1-N(2)-C(3)	99.0(3)
C(7)-C(8)	1.555(5)	C(2)-N(2)-Pd(1)	109.9(3)
		C(2)#1-N(2)-Pd(1)	109.9(3)
		C(3)-N(2)-Pd(1)	107.3(3)
		N(2)-C(3)-C(8)	109.9(4)
		N(2)-C(3)-C(4)	113.0(4)
		C(8)-C(3)-C(4)	110.5(3)
		C(5)-C(4)-C(3)	111.6(4)
		C(6)-C(5)-C(4)	107.6(6)
		C(5)-C(6)-C(7)	109.3(7)
		C(6)-C(7)-C(8)	109.5(5)
		N(1)-C(8)-C(3)	109.5(4)
		N(1)-C(8)-C(7)	112.1(4)
		C(3)-C(8)-C(7)	109.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,z

Table S5. Anisotropic displacement parameters ($Å^2 x 10^4$) for 1b (CCDC 263612). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	169(1)	235(1)	130(1)	10(5)	0	0
N(1)	340(20)	185(13)	200(20)	15(15)	0	0
N(2)	300(20)	172(15)	180(20)	29(12)	0	0
C(1)	470(20)	760(30)	480(20)	-280(20)	59(19)	-310(20)
C(2)	650(30)	750(30)	610(30)	320(20)	200(20)	460(20)
C(3)	170(20)	215(15)	150(19)	24(14)	-21(15)	10(12)
C(4)	380(20)	299(16)	236(19)	97(15)	0	0
C(5)	290(20)	520(20)	250(30)	220(40)	-50(40)	-55(17)
C(6)	304(19)	520(20)	145(16)	90(70)	-10(70)	-35(17)
C(7)	400(20)	304(16)	180(17)	-57(14)	0	0
C(8)	191(19)	224(16)	125(18)	3(15)	28(15)	-21(13)
C(9)	340(30)	390(30)	260(30)	130(20)	0	0
C(10)	320(30)	420(40)	250(30)	-90(20)	0	0